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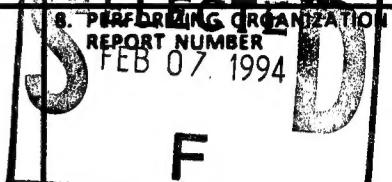
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12a. DISTRIBUTION/AVAILABILITY STATEMENT

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3. ABSTRACT (Maximum 200 words) The fact that the three nitrogen atoms present in urazole and appropriately substituted urazoles have been shown to possess substantial bond-making reactivities has prompted our investigations of (a) the stabilities of nitrogen-centered anions and radicals derived from substituted urazoles; (b) issues related to the syntheses of selected urazole monomers; and (c) the properties of a number of polymers that contain urazoles as monomeric subunits. Published discoveries from this project include (i) determinations of acidity constants for urazole and substituted urazoles in dimethyl sulfoxide as well as aqueous solutions; (ii) evaluations of the N-H homolytic bond strengths in urazole, substituted urazoles, and related heterocycles; and (iii) determinations of the reaction products that result when 1-phenylurazole is subjected to conditions that result in its methylation. Unpublished results from this project include (i) synthesis of various dinitro- and diaminourazoles (useful urazole monomers); (ii) synthesis of polyurazole-ketones; (iii) synthesis of polyurazole epoxies; (iv) synthesis of polyurazole-imides; and (v) characterization of the aforementioned polymers. The newly-synthesized polyurazoles were shown to be insoluble in chlorinated organic solvents but were found to be sparingly soluble in DMSO. The polyurazole-ketones and polyurazole epoxies had T_g 's of about 260°C.

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PREPARATION AND STUDIES OF URAZOLE-CONTAINING POLYMERS

FINAL REPORT

DR. MARK J. BAUSCH

U.S. ARMY RESEARCH OFFICE

DAAL-03-90-G-0046

SOUTHERN ILLINOIS UNIVERSITY CARBONDALE

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FINAL REPORT

FIFTY COPIES REQUIRED

1. ARO PROPOSAL NUMBER: 27445-CH
2. PERIOD COVERED BY REPORT: January 15 1990-December 31, 1991
3. TITLE OF PROPOSAL: "Preparation and Studies of Urazole-Containing Polymers"
4. CONTRACT OR GRANT NUMBER: #DAAL-03-90-G-0046
5. NAME OF INSTITUTION: Southern Illinois University-Carbondale
6. AUTHOR(S) OF REPORT: M. J. Bausch
7. LIST OF MANUSCRIPTS PUBLISHED UNDER ARO SPONSORSHIP DURING THIS PERIOD, INCLUDING JOURNAL REFERENCES:
 - A."Dimethyl Sulfoxide Phase N-H Equilibrium Acidities for Urazole and Substituted Urazoles: For Urazole and 1-Substituted Urazoles, Which Proton is More Acidic?," Bausch, M.J.; David, B.; Dobrowolski, P.; Prasad, V. *J. Org. Chem.* **1990**, *55*, 5806-5808.
 - B."Potentiometric and Spectroscopic Investigations of the Aqueous Phase Acid-Base Chemistry of Urazole and Substituted Urazoles," Bausch, M.J.; Selmarten, D.; Gostowski, R.; Dobrowolski, P. *J. Phys. Org. Chem.* **1991**, *4*, 67-69.
 - C."Proton Transfer Chemistry of Urazoles and Related Imides, Amides, and Diacylhydrazides," Bausch, M.J.; David, B.; Dobrowolski, P.; Guadalupe-Fasano, C.; Gostowski, R.; Selmarten, D.; Prasad, V.; Vaughn, A.; Wang, L.-H. *J. Org. Chem.* **1991**, *56*, 5643-5651.
 - D."Relative Homolytic Strengths of N-H Bonds in Cyclic and Acyclic Diacylhydrazides, Imides, and Hydrazoic Acid," Bausch, M.J.; David, B.; Prasad, V.; Vaughn, A.; Wang, L.-H. *J. Phys. Org. Chem.* **1992**, *5*, 1-6.
 - E."Proton, Electron, and Hydrogen Atom Transfers of Ions, Radicals, and Radical Ions Derived from Substituted Urazoles and Triazolinediones," Bausch, M.J.; David, B. *J. Org. Chem.* **1992**, *57*, 1118-1124.
 - F."A Reinvestigation of the Reactions Between Diazomethane and 1-Phenylurazole," Bausch, M.J.; Wang, L.-H. *J. Phys. Org. Chem.* **1993**, *6*, 601-608.
8. SCIENTIFIC PERSONNEL SUPPORTED BY THIS PROJECT AND DEGREES AWARDED DURING THIS REPORTING PERIOD:
 - R. Gostowski (graduate student)
 - L. Wang (graduate student)

SUMMARY OF RESEARCH FINDINGS

Four major experimental areas (shown as 1-4 below) were outlined in our proposal entitled "Preparation and Studies of Urazole-Containing Polymers". Summaries of our findings in each area is shown below.

(1) Determinations of Acidity Constants for Substituted Urazoles and Their Conjugate Bases, and Studies of the Kinetics of the Reactions of Urazole Anions with Relevant Monomers

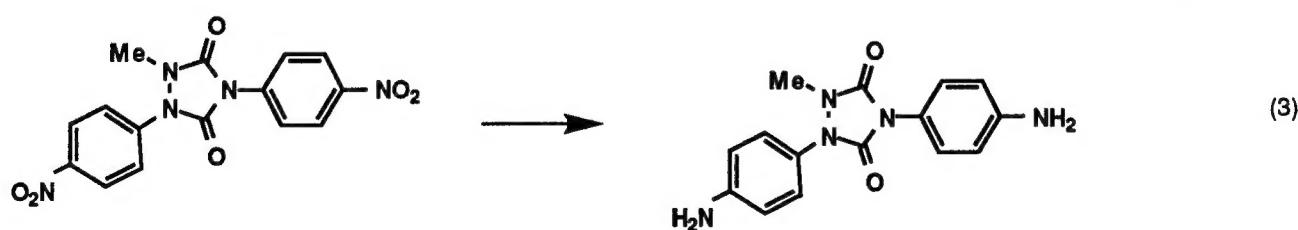
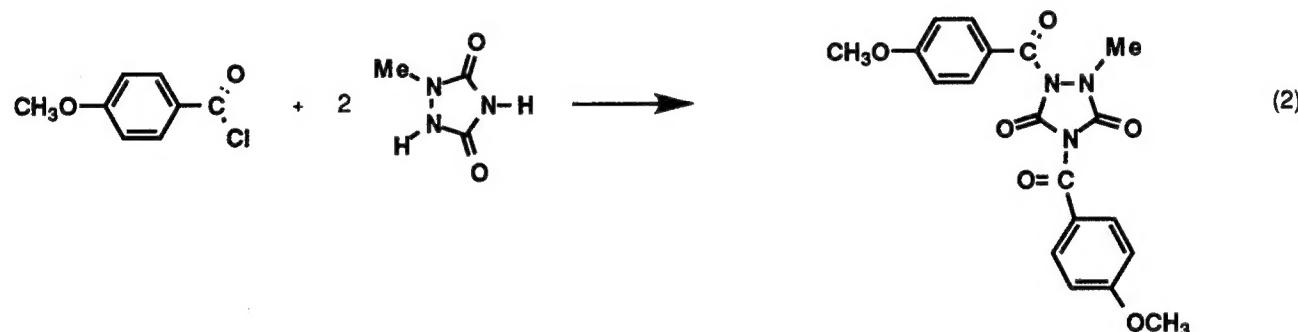
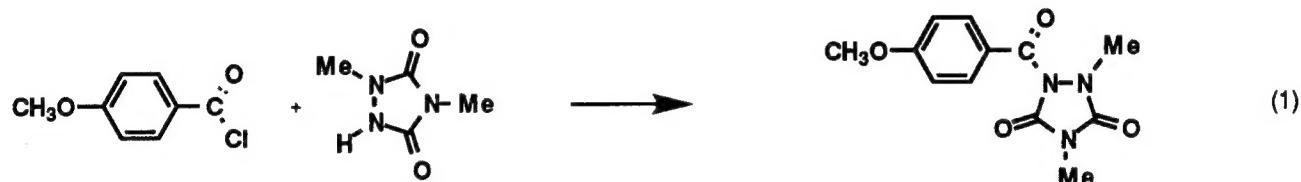
Publications A, B, C, D, and E listed on the previous page outline the tangible results of our efforts in this area.

(2) Synthesis of Urazole-Containing Monomers, Model Reactions, and Polymers

(a) Urazole-Containing Monomers and Model Reactions

Publication F listed on the previous page outlines some of the urazole-related monomer syntheses work.

In unpublished work, Equations 1-3 describe the preparation of additional urazole monomers or urazole polymer model compounds

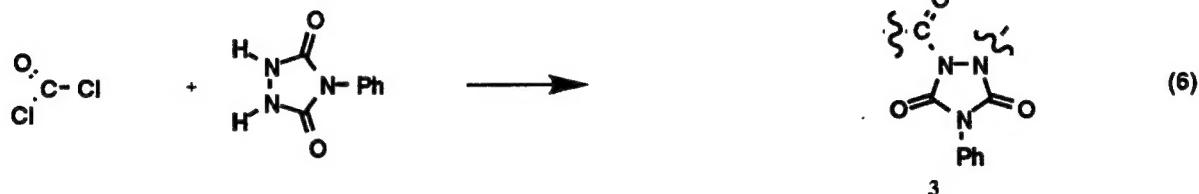
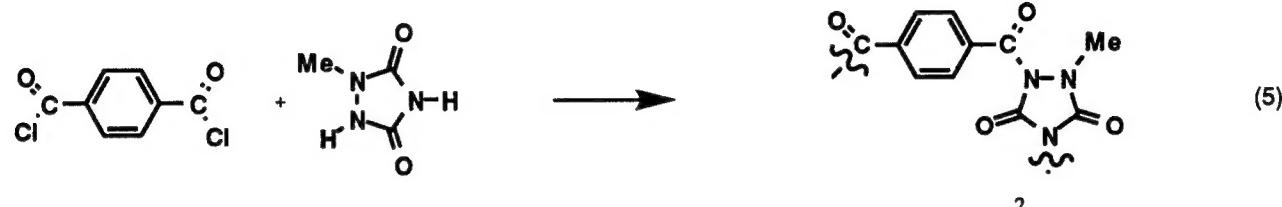
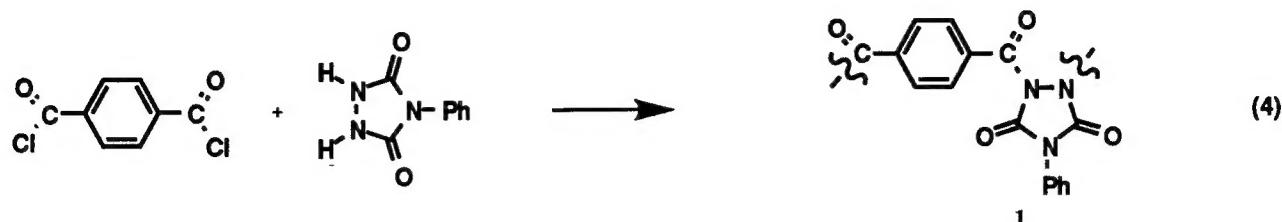


The reactions depicted in equations 1 and 2 were carried out in the presence of pyridine; the product structures were confirmed by their ^1H NMR spectra. The pyridine hydrochloride formed in these reactions was removed by washing the crude solid product with water. The hydrogenation in equation 3 was carried out in the presence of Pd/C as a catalyst.

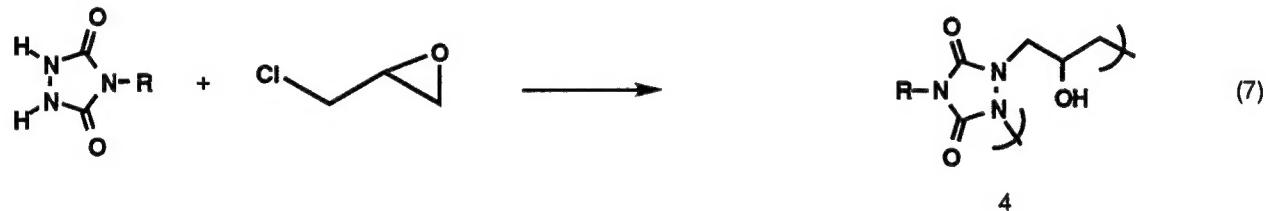
(b) Urazole-Containing Polymers

Equations 4-8 describe the unpublished preparations of urazole-containing polymers **1-5**:

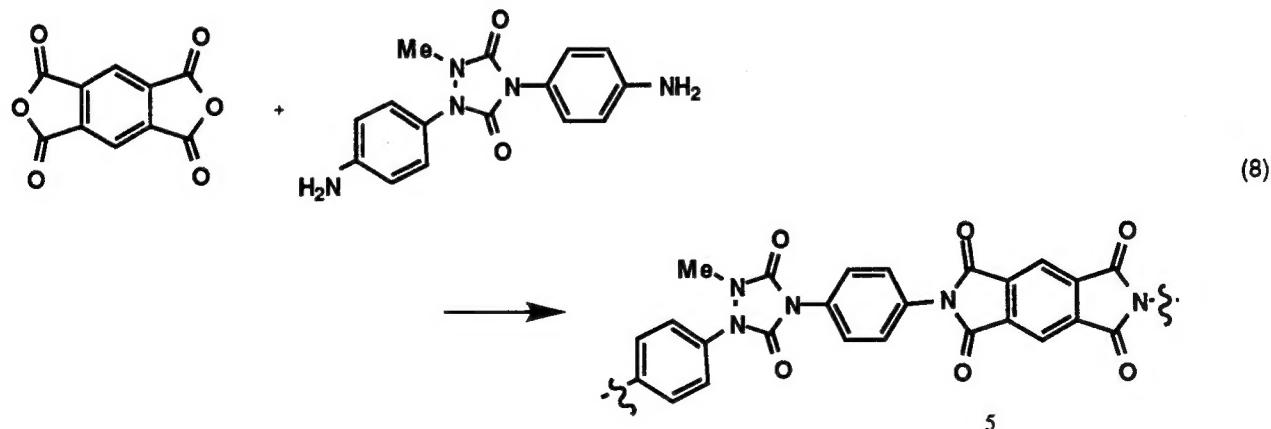
(i) Polyurazole-ketones



(ii) Polyurazole-epoxides



(iii) Polyurazole-imides



Successful preparation of polyurazole-ketones **1-3** is highly sensitive to the base chosen for the reaction. The

polymerizations depicted in equations 1 and 2 proceeded efficiently when performed when an excess amount of base (i.e. pyridine or triethyl amine) were present. This is likely due to the fact that basic conditions are likely to enhance not only the nucleophilicity of neutral urazole monomers but also the reactivity of the chosen acid chloride.

Polymer **4** is an example of a new class of urazole-containing epoxy resin. The reaction depicted in eq 7 was carried out in the presence of sodium hydroxide, at 100°C. During the addition of the aqueous sodium hydroxide, the reaction mixture was stirred vigorously. When the reaction was complete, a taffy-like material rose to the top of the reaction mixture. The resinous material was washed with hot water and heated at 100°C to remove water.

Polymer **5** is an example of a polyimide. The reaction depicted in eq 8 was found to proceed smoothly under relatively mild conditions, using N,N-dimethylacetamide as solvent.

•Evaluation of Urazole-Containing Polymers

Polymers **1-3** are insoluble in chlorinated organic solvents such as chloroform and methylene chloride. They are sparingly soluble in DMSO, which enabled their NMR evaluation in DMSO-d₆. We have been unable to collect precise molecular weight analyses for **1-3**. Polymers **1** and **2**, when prepared in toluene with pyridine used as a base, were shown to have T_g's at about 260°C. No reliable DSC data were obtained for polymers **4** or **5**.

•Studies of Possible Crosslinking Reactions of Polymers that Contain Urazoles

All attempts to "thermoset" urazole-containing thermoplastics **1-3** and **5** were unsuccessful.